



# Effect of catalyst precursor and its pretreatment on the amount of $\beta$ -Pd hydride phase and HDS activity of Pd-Pt/silica-alumina



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## ABSTRACT

The effect of catalyst precursor and pretreatment on the content of  $\beta$ -Pd hydride ( $\text{PdH}_x$ ) and activity of the reduced bimetallic Pd-Pt catalysts in hydrodesulfurization (HDS) of thiophene and benzothiophene was studied. The catalysts prepared by co-impregnation of mesoporous silica-alumina (MSA) by different metal compounds were characterized by nitrogen, hydrogen, CO adsorption, chemical analyses, electron-probe microanalysis (EPMA) and temperature-programmed hydride decomposition (TPHD). It was found that metal precursor and its pretreatment greatly affected the properties of the catalysts. The most active catalysts were prepared from Pd acetate and  $\text{Pt}(\text{NH}_3)_4(\text{OH})_2$ . Strong Brønsted acidity of the support led to the highly active and sulfur tolerant catalysts. About 20% of the active phase surface remained in the metallic state after thiophene HDS. The reduced Pd-Pt/MSA catalysts absorbed hydrogen in the form of  $\text{PdH}_x$  phase. Its amount was greatly affected by the precursor, its pretreatment and overall metal dispersion. A relation between thiophene HDS activity and the amount of hydrogen present in the  $\text{PdH}_x$  was observed within the whole series of Pd-Pt catalysts. This shows that the hydrogen accumulated in the bulk of Pd participated in the reaction along with the hydrogen activated on the catalyst surface and positively contributed to the overall thiophene transformation over Pd-Pt/MSA catalysts.

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## 1. Introduction

Bimetallic catalysts containing Pd and Pt have primarily been studied for the purposes of hydrodearomatization of industrial feeds and hydrogenation (HYD) of aromatic model compounds in the presence of sulfur [1–6]. Parallel to this research, some studies have also been devoted to their evaluation in hydrodesulfurization (HDS) reactions of simple model compounds such as thiophene or dibenzothiophene [7,8] and for the deep HDS of substituted dibenzothiophenes [4,8,9]. This is because these catalysts show high HYD activity which allows via HYD route the easier transformation of refractory sulfur molecules. Metallic Pd-Pt phase is usually deposited on acidic supports, mostly USY zeolite and amorphous silica-alumina, favorable for the higher electron-deficiency of the noble metals which reflects in the better sulfur tolerance and catalysts activity. These catalysts are often prepared from simple metal chlorides or different complexes of Pd and Pt by co-impregnation, mostly followed by calcination in air and reduction by hydrogen at 300–500 °C.

Recently, we have studied monometallic Pt catalysts [10] as well as monometallic Pd and bimetallic Pd-Pt catalysts [11] in HDS of thiophene and benzothiophene. In both cases, catalysts supports were mesoporous silica-aluminas (MSA) with acidities enhanced by the post-syntheses acid leaching. Such modified supports impregnated with suitable noble metal compounds gave very active monometallic catalysts. The highest thiophene activities were achieved with Pt and Pd catalysts prepared from  $\text{Pt}(\text{NH}_3)_4(\text{OH})_2$  and Pd acetate, respectively. In the next, co-impregnation of modified MSA by these compounds resulted in a highly active bimetallic Pd-Pt/MSA catalyst that showed significant synergistic effect and exceeded in thiophene and benzothiophene transformations the activities of a conventional sulfide CoMo/alumina catalyst. An interesting property of the reduced Pd-Pt/MSA catalyst was a considerable amount of hydrogen present in the form of  $\beta$ -Pd hydride ( $\text{PdH}_x$ ). This was revealed during characterization of this catalyst by TPD technique and led us to assume that the high activity of this sample could be in a relation to the absorbed hydrogen [11].

There are several examples of the catalytic role of the hydrogen absorbed in the bulk of Pd. Positive effects of the  $\text{PdH}_x$  in a metallic Pd and a reduced Pd/alumina catalyst on the rate of HYD of acetylene, ethene, and butadiene have been found by different research groups [12–14]. Hydrodechlorination of chlorofluorocarbons over

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Pd(111) crystal proceeded even in the absence of gaseous hydrogen and was ascribed to the participation of solid state hydrogen [15]. Similarly, the participation of a subsurface hydrogen in HYD of 1-pentene and 1-pentyne over Pd black was described by Teschner et al. [16] and the influence of Pd hydride on the selectivity of HYD of benzonitrile was confirmed by Bakker et al. [17]. However, all these studies concerned only Pd and to our best knowledge, there are not analogous studies concerning bimetallic Pd-Pt system or a similar study related to HDS reaction.

It is well known that the formation of  $\text{PdH}_x$  in supported Pd catalysts is strongly affected by the size of the metal particles [18–20]. Metal dispersion in Pd/silica catalysts can be influenced by thermal pretreatment of the catalyst precursors in different gas atmosphere (He,  $\text{H}_2$ ,  $\text{O}_2$ ) [21,22]. In addition, annealing at temperatures above 400 °C, may lead to the interaction of Pd with  $\text{SiO}_2$  forming Pd silicide that hinders the formation of  $\text{PdH}_x$  [23]. In order to check a possible role of  $\text{PdH}_x$  in our Pd-Pt/MSA samples, we made use of the above findings and pretreated the catalyst precursors in different ways so as to obtain a broader series of catalysts with different content of  $\text{PdH}_x$ . This should make it easier to see whether the activity changes could be compared with the hydrogen content in the catalysts.

Two main goals of this work can be summarized as follows. The first, from an application point of view it seemed useful to find if the activity of Pd-Pt/MSA catalyst prepared from Pd acetate and  $\text{Pt}(\text{NH}_3)_4(\text{OH})_2$  can further be improved by some simple way, for example by the different pretreatment of its precursor. The second aim was an attempt to find if there is a relation between HDS activity of the catalysts and the hydrogen content in  $\text{PdH}_x$  phase. Because both noble metal compounds mentioned above are not the most frequently used, also other catalyst precursors, prepared from commonly used  $\text{PdCl}_2$  and  $\text{H}_2\text{PtCl}_6$  were included for comparison.

## 2. Experimental

### 2.1. Preparation of the support and catalysts

Mesoporous silica-alumina (MSA) modified by post-synthesis extraction by nitric acid was used in the form of 0.16–0.315 mm particles as a catalyst support. The acid extraction eliminated the originally present extra-framework non-acidic  $\text{Al}_{\text{oct}}$  forms and the modified support was thus substantially enriched by  $\text{Al}_{\text{tet}}$  species. It contained 91 wt.%  $\text{SiO}_2$ , 9 wt.%  $\text{Al}_2\text{O}_3$  and possessed the BET surface area of 643  $\text{m}^2/\text{g}$ . Extraction led to enhancement of strong Brønsted acidity, proven by catalytic tests in skeletal isomerization of cyclohexene and cracking of cumene [11].

Two catalyst precursors were prepared by co-impregnation of the modified MSA with solutions of Pd acetate +  $\text{Pt}(\text{NH}_3)_4(\text{OH})_2$  and Pd acetate +  $\text{H}_2\text{PtCl}_6$ . Acetone solution of Pd acetate was mixed with aqueous solution of  $\text{Pt}(\text{NH}_3)_4(\text{OH})_2$  (or  $\text{H}_2\text{PtCl}_6$ ) giving a mixture (1:1). The third precursor was prepared similarly from aqueous solution of  $\text{PdCl}_2 + \text{H}_2\text{PtCl}_6$ . In these solutions, we assume the presence of non-dissociated Pd acetate, while cationic  $\text{Pt}(\text{NH}_3)_4^{2+}$  species and  $\text{PtCl}_6^{2-}$  and  $\text{PdCl}_4^{2-}$  anions. The three combinations used gave homogeneous solutions and no precipitation was observed.

The slurries were evaporated to dryness at 60 °C under vacuum in a rotary evaporator and the solids were dried at 120 °C on air. They were either directly reduced by hydrogen (symbol H) or calcined in helium or air (symbols He and Ox, respectively) at 300–600 °C prior to their reduction in hydrogen. The symbols PdA, PdC, PtO and PtC stand for Pd acetate,  $\text{PdCl}_2$ ,  $\text{Pt}(\text{NH}_3)_4(\text{OH})_2$  and  $\text{H}_2\text{PtCl}_6$ , respectively. The bimetallic catalyst precursors are denoted accordingly, as PdA-PtO, PdA-PtC and PdC-PtC.

The pretreatment temperature is given by a number behind the symbol for gas.

### 2.2. Characterization of the catalysts

The chemical composition of the catalysts was determined by inductively coupled plasma-atomic absorption spectroscopy (ICP/AAS). BET surface areas and pore-size distributions of the samples degassed at 400 °C were determined by nitrogen adsorption with an ASAP2010 M instrument (Micromeritics). Metal dispersions were determined by pulse hydrogen adsorption at 22 °C in an apparatus equipped with thermal conductivity detector (TCD) [24]. The catalyst (40–80 mg) was reduced by hydrogen at 300 or 400 °C for 1 h, purged by nitrogen at the same temperature for 0.5 h, and cooled to 22 °C. Then it was titrated by 10  $\mu\text{l}$  pulses of hydrogen. The H:Pd = 1:1 and H:Pt = 1:1 stoichiometries were adopted for the calculation of Pd and Pt dispersions according to Anderson and Pratt [25]. In addition, the metal dispersions of two samples were determined by CO adsorption on a commercial Autochem 2920 instrument (Micromeritics). 40 mg of a catalyst sample was reduced by 5% hydrogen in argon at 300 or 400 °C, purged by helium at the same temperature for 1 h and cooled to 0 °C in helium. The catalysts were then titrated by pulses of 5% CO in helium. The CO:Pd = 1:2 and the CO:Pt = 1:1 stoichiometries were adopted for the calculation of Pd and Pt dispersions, respectively [18,20,25,27]. The overall dispersion of the Pd-Pt catalysts was calculated by using the above stoichiometries and taking into account the molar fractions of the metals in the catalysts. The dispersion was expressed by  $\text{H}/(\text{Pd} + \text{Pt})$  or  $\text{CO}/(\text{Pd} + \text{Pt})$  atomic ratios. The sulfur coverage of the active metal phase is usually calculated as  $\Theta_S = (D_R - D_S)/D_R$ , where  $D_R$  and  $D_S$  are dispersions or gas uptakes (CO, hydrogen) on the reduced and sulfided metals, respectively [4,26]. In the present work,  $D_R$  and  $D_S$  mean the dispersions prior to and after thiophene HDS test, respectively.

The amount of the hydrogen absorbed in  $\text{PdH}_x$  was evaluated by temperature-programmed hydride decomposition (TPHD) by a procedure analogous to that used by Pinna et al. [18]. TPHD was carried out in the same apparatus as used for hydrogen adsorption. The catalysts (60–200 mg) were in situ re-reduced by hydrogen at 300 or 400 °C for 0.5 h, cooled in hydrogen to room temperature and purged with a mixture of 5%  $\text{H}_2$  in argon (35 ml/min) for 0.5 h. Then the temperature was raised to 140 °C (ramp 15 °C/min) in a hydrogen/argon mixture and the amount of desorbed hydrogen was monitored by TCD. The amounts of hydrogen released between 55 °C and 95 °C were taken as corresponding to the  $\text{PdH}_x$  decomposition [19].

The electron probe micro-analysis (EPMA) was performed on a SX-100 Instrument (Cameca, France). The reduced catalysts particles were mounted on a 1-inch epoxy disc, polished to expose their cross-section area and coated with thin layer of gold. The W cathode at 15 kV and back-scattered electron mode was used during measurements. Several images and point analyses were taken for each catalyst sample.

### 2.3. Catalytic tests

#### 2.3.1. Thiophene HDS

The activity of the catalysts in HDS of thiophene (TH) was evaluated in a flow microreactor with a fixed catalyst bed at 280 °C and 2 MPa, as described in detail previously [11]. The feed contained 240 ppm of TH in hydrogen (150 ml/min). The flow rate  $F_{\text{TH}}$  was constant ( $9.7 \times 10^{-5} \text{ mol}_{\text{TH}}/\text{h}$ ) and the catalyst amount W was close to 10 mg. The catalysts were in situ re-activated by hydrogen reduction at 300 or 400 °C for 1 h before reaction, which was usually carried out 4–6 h on stream. The on-line analyses were carried out on a GC HP 5890 equipped with FID detector and a 3.5 m packed

**Table 1**  
Composition of Pd-Pt/MSA catalysts.

Catalyst precursor	Metal content (wt.%)		Atomic ratio Pd:Pt	Surface area (m <sup>2</sup> /g)
	Pd	Pt		
PdA-PtO	0.38	0.35	2.0	564
PdA-PtC	0.66	0.41	3.0	564
PdC-PtC	0.68	0.45	2.8	562

column (Carbopack B 60/80 4% Carbowax 20 M) at 125 °C. The reaction products were C<sub>4</sub> hydrocarbons, H<sub>2</sub>S and tetrahydrothiophene (THT). The activities were expressed by overall TH conversions,  $x_{\text{TH}}$ , conversions in THT,  $x_{\text{THT}}$ , conversions in C<sub>4</sub> hydrocarbons,  $x_{\text{C4}}$  and by the pseudo-first-order rate constants  $k_{\text{TH}}$  for TH disappearance calculated according to  $k_{\text{TH}} = -(F_{\text{TH}}/W) \ln (1 - x_{\text{TH}})$  and given per weight unit of the catalyst.

### 2.3.2. Benzothiophene HDS

The activity of selected catalysts in HDS of benzothiophene (BT) was evaluated in the gas phase in a flow reactor with a fixed bed of the catalyst at 330 °C and 1.6 MPa, as described in detail previously [11]. The rate of the feed  $F_{\text{BT}}$  was  $7.7 \times 10^{-3}$  mol<sub>BT</sub>/h and the composition was 16 kPa, 200 kPa and 1384 kPa of BT, n-decane and hydrogen, respectively. The catalyst was in situ re-activated by hydrogen at 400 °C for 1 h before the reaction. The samples of the condensed reaction mixture were analyzed on a GC HP 6890 with a 30 m capillary HP-5 column (0.53 mm) using a temperature program between 130–180 °C. The products were ethylbenzene (EB), H<sub>2</sub>S and dihydrobenzothiophene (DHBT). The activities after 3 h on stream were expressed by overall BT conversions  $x_{\text{BT}}$ , conversions to DHBT,  $x_{\text{DHBT}}$  and conversions to EB,  $x_{\text{EB}}$ . The rate constants  $k_{\text{BT}}$  for the overall BT transformation were calculated analogously as those for TH.

## 3. Results and discussion

### 3.1. Characterization and properties of Pd-Pt/MSA catalysts

The composition of the catalysts is given in Table 1. The overall metal loading was between 0.7–1.1 wt.%, which is usually optimal to achieve a good metal dispersion and catalytic activity. Pd was the predominant metal in all samples. The lower Pd:Pt ratio in PdA-PtO precursor shows on certain enrichment by Pt (34 mol.%) as compared to PdA-PtC and PdC-PtC samples (~25 mol.%). Deposition of Pd and Pt on MSA led to a small decrease of the BET surface area of the support and all the catalysts showed almost the same values, irrespective of the precursor used.

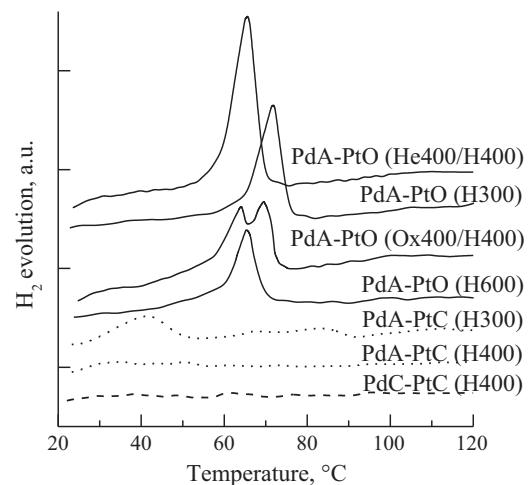
**Table 2**

Effect of pretreatment on overall metal dispersion and molar fraction of hydrogen in PdH<sub>x</sub> phase.

Catalyst precursor	Pretreatment (gas/°C)	H/(Pd + Pt)	$x = \text{H}/\text{Pd}$
PdA-PtO	H300	0.53	0.228
	H400	0.68 (0.12) <sup>a</sup>	0.253
	H550	0.88	0.135
	H600	0.68	0.123
	Ox400/H400	1.34 (0.50) <sup>b</sup>	0.188
	He400/H400	0.29	0.285
PdA-PtC	H300	0.40	0.085
	H400	0.59	0.029
	He300/H300	2.24 (0.21) <sup>b</sup>	0.071
PdC-PtC	H400	0.15	0.017
	Ox500/H400	1.50	0.042

<sup>a</sup> After 5 h thiophene HDS run.

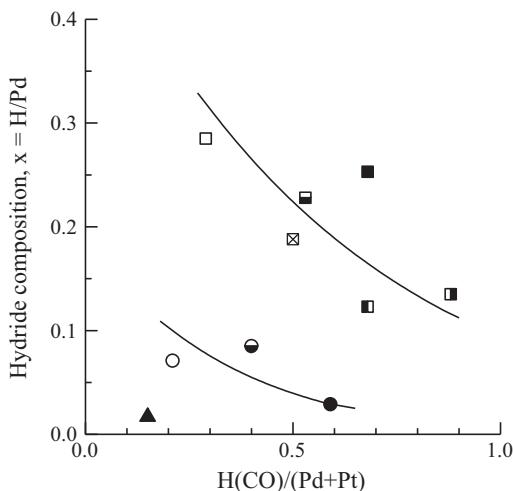
<sup>b</sup> Determined by CO sorption as CO/(Pd + Pt).



**Fig. 1.** Temperature-programmed hydride decomposition (TPHD) in some Pd-Pt/MSA catalysts.

Table 2 shows the overall metal dispersion of the catalysts pretreated by different ways. These values were satisfactory for the majority of the catalysts while the distinctly low for one sample prepared by the direct reduction of PdC-PtC. On the other hand, three catalysts showed the H/(Pd + Pt) ratios considerably exceeding unity. This anomalous behavior, which was also observed on a Pt/MSA catalyst in our recent work [10], can be ascribed to hydrogen spillover. In these cases, the additionally performed CO sorption gave reasonable dispersion values, which were further considered as representative. However, this could not be done with the pre-oxidized PdC-PtC, that was available in the amount not sufficient for such a measurement. As also seen from Table 2, the metal dispersion is not influenced only by the precursor, but also by the gas environment and temperature. Within the group of the reduced PdA-PtO catalysts, the dispersion goes through a maximum at the reduction temperature of 550 °C. In case of pre-oxidation or helium treatment, the originally formed adsorbed oxo-species are transformed to metal particles by subsequent reduction. It is interesting, that the pretreatment of two precursors in helium gave always lower dispersions (PdA-PtO and PdA-PtC).

It is well known that the catalysts containing Pd can absorb hydrogen in the bulk of the metal phase in the form of  $\beta$ -Pd hydride (PdH<sub>x</sub>). Its thermal decomposition can be monitored by TPHD up to around 100 °C at atmospheric pressure [18,19]. The TPHD patterns of the selected Pd-Pt catalysts, normalized to the same weight amount, are shown as examples in Fig. 1. The largest hydrogen evolution was found on the catalysts prepared from the PdA-PtO precursor. Substantially lower or almost zero hydrogen desorptions were observed on the catalysts prepared from the other precursors. The TPHD maxima little varied in dependence on the catalyst pretreatment. In some cases, two maxima were observed. Such a case was observed recently over Pd/SiO<sub>2</sub> catalysts by Bonarowska et al. [19] and was ascribed to a bimodal distribution of the size of the metal particles. The Pd-Pt catalyst prepared from PdA-PtC by reduction at 300 °C gave a more complicated pattern suggesting also the desorption of chemisorbed hydrogen, similarly as observed for the monometallic Pd/MSA catalyst in our preceding work [11]. The amounts of desorbed hydrogen that reflect the composition of PdH<sub>x</sub> phase are expressed by molar ratios  $x = \text{H}/\text{Pd}$  and are listed in Table 2. As expected, the greatest  $x$  values were found for the series of the catalysts prepared from PdA-PtO. The limiting amount of hydrogen absorbed in the bulk of the large Pd particles is close to  $x = 0.6$  [19]. Then the catalysts prepared from PdA-PtO approach around 20–50% of this value.



**Fig. 2.** Composition of Pd hydride phase as a function of overall metal dispersion. PdA-PtO; H 300 (■), H 400 (■), H 550 (□), H 600 (□), He 400/H400 (□), Ox 400/H400 (□). PdA-PtC; H 400 (●), H 300 (●), He 300/H300 (○). PdC-PtC; H 400 (▲).

It has well been documented in the literature that the ability of the Pd phase to absorb hydrogen diminishes at higher Pd dispersion [18–20] and also by alloying with Pt. Maximum Pt content in the Pd-Pt alloy limiting the Pd hydride formation is around  $X_{\text{Pt}} = 0.12$  [28 and References therein]. It can be assumed that both factors can play role in the present work. Fig. 2 shows the relation between the molar fraction of hydrogen  $x = \text{H/Pd}$  and the overall metal dispersion of Pd-Pt/MSA catalysts. For both PdA-PtO and PdA-PtC precursors, decreasing trends at higher dispersion are well apparent, which shows that the bimetallic Pd-Pt/MSA catalysts behave similarly as monometallic Pd catalysts. This data suggests that some part of Pd in the Pd-Pt catalysts is present either as isolated metal particles or the less alloyed with Pt. This effect is more pronounced for the PdA-PtO catalysts series.

The extent of the Pd-Pt alloy formation in the bimetallic catalysts seems to be significantly influenced by the starting noble metal compounds. Pawelec et al. [3] found the alloy in the catalyst prepared from  $\text{H}_2\text{PdCl}_4$  and  $\text{H}_2\text{PtCl}_6$ , while only isolated Pd and Pt particles were present when Pd nitrate and Pt tetraamine nitrate were used. In homogeneous water/ethanol solution, formation of bimetallic Pd-Pt clusters proceeds from  $\text{PdCl}_2$  and  $\text{H}_2\text{PtCl}_6$  easily already at  $90^\circ\text{C}$  [29]. The same metal compounds deposited on silica-alumina and silica gave a Pd-Pt alloy by reduction [2,30]. On the other hand, both alloy and monometallic Pd particles were formed when Pd and Pt tetraamine carbonates and tetraamine nitrates were employed. The formation of monometallic Pd particles on Y zeolite obviously occurs at the higher Pd:Pt ratio [31], and the fraction of the monometallic Pd aggregates on a silica-alumina approaches 41% [5]. These data suggest that the presence of Pd-Pt alloy can almost certainly be expected when metal chlorides are used as precursors, while the isolated Pd and Pt particles or Pd particles coexisting with the alloy can be formed when different or chlorine-free metal compounds are used. The results obtained in the present work agree well with these conclusions. The samples prepared from PdA-PtO show lower Pd:Pt = 2 ratio than the catalysts originating from the two remaining precursors (Pd:Pt = 2.8 and 3). One can speculate that the former catalysts should contain less free Pd fraction able to create  $\text{PdH}_x$  phase. However, data in Table 2 show the opposite. The PdA-PtO series absorbed more  $\text{H}_2$  than PdA-PtC and PdC-PtC which confirms less alloyed bimetallic phases or higher proportion of isolated Pd particles. This result is in accordance with the literature and shows the overwhelming effect

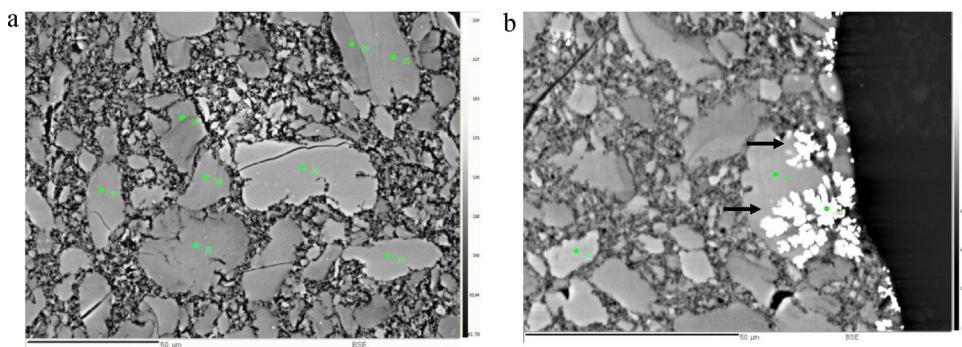
of the nature of precursor in our catalysts over only minor effect of the Pd:Pt ratio.

The results of EPMA measurements are shown in Fig. 3. Fig. 3a shows the micrograph of the surface of the catalyst prepared from PdA-PtO by reduction at  $400^\circ\text{C}$  as an image typical for almost all the catalysts. The only exception was the catalyst prepared from PdC-PtC by direct reduction (Fig. 3b). Distinct pale regions greatly enriched by Pd and Pt were found for this sample in the vicinity of the geometrical surface of the particles. The point analyses of these regions revealed that contain around 60% of the metallic phase and 40% of the support. Moreover, these regions showed atomic Pd:Pt ratio close to 3.8 and the presence of residual chlorine (0.9% Cl). It is clear that the pretreatment of PdC-PtC in hydrogen led to a segregation of  $\text{PdCl}_2$  and  $\text{H}_2\text{PtCl}_6$  on the surface of MSA followed by massive metal sintering. This conclusion is in agreement with the low metal dispersion of 0.15 found by hydrogen sorption and explains a metallic-gray color of this sample after the reduction. It is known that weak interactions of  $\text{PdCl}_2$  and  $\text{H}_2\text{PtCl}_6$  with silica can lead to less dispersed metals after direct reduction [22,32]. This is most likely the reason for sintering of both metals on the MSA support with high silica content. On the other hand, the catalyst prepared from PdC-PtC by pre-oxidation in air at  $500^\circ\text{C}$  showed a brown color typical of the other samples and higher  $\text{H}/(\text{Pd} + \text{Pt})$  ratio. The EPMA image was similar to that in Fig. 3a and chlorine was not detected in this sample. In this case, the pre-oxidation treatment led to the well dispersed and active catalyst. This can be ascribed to the reaction of metal chlorides with surface OH groups forming anchored oxo-chloride species, giving well dispersed metallic phase by reduction [22]. As far as the content of chlorine in two remaining catalysts is concerned, EPMA analysis of PdA-PtC revealed the spot with local concentration 0.6% Cl while in PdA-PtO confirmed the chlorine absence. These analyses show on increasing chlorine contents in the order: PdA-PtO ~ PdC-PtC (pre-oxidized) < PdA-PtC < PdC-PtC, which evokes an idea about its negative effect on  $\text{PdH}_x$  formation. Various factors have been shown to diminish the formation of  $\text{PdH}_x$ , such as higher Pd dispersion [18–20], alloying with Pt [28] or formation of Pd silicide [23]. However, up to now there is no study reporting the inhibition of  $\text{PdH}_x$  formation by chlorine persisting on the catalysts. We assume therefore this reason less probable, although definitely cannot be ruled out.

Besides the  $\text{PdH}_x$  content and EPMA analyses, we have at present no additional data giving information about the extent of alloying of both metals in our Pd-Pt/MSA catalysts. Nevertheless, some conclusions can be drawn. The Pd-Pt alloy is undoubtedly formed in the directly reduced PdC-PtC catalyst. Previous findings of other authors on the alloy formation by reduction from  $\text{PdCl}_2$  and  $\text{H}_2\text{PtCl}_6$  [2,3,30] suggest the presence of alloy also in our pre-oxidized PdC-PtC catalyst. This assumption is further supported by its very low  $\text{PdH}_x$  content (Table 2). As to the other PdA-PtO and PdA-PtC catalysts, their higher  $\text{PdH}_x$  contents point out to much smaller alloy amounts than in PdC-PtC. This result is in a good accordance with the earlier observations that showed that Pd and Pt compounds other than chlorides usually gave no alloy [3] or the less alloy accompanied by monometallic Pd particles [5,31].

### 3.2. Activity in HDS of thiophene and benzothiophene

The conversion data for the reaction of TH and the rate constants  $k_{\text{TH}}$  are listed for Pd-Pt/MSA catalysts in Table 3. The HDS was accompanied by a significant formation of an intermediate THT. This can be ascribed to hydrogenating character of supported metals at higher hydrogen pressure of 2 MPa [33,34]. It is worth to mention that THT amount was substantially lower on the catalysts of PdA-PtO series, giving a highest selectivity in desulfurized products,  $\text{C}_4$  hydrocarbons. This finding seems to be consistent with



**Fig. 3.** Back-scattered electron images of Pd-Pt/MSA catalysts prepared by direct reduction at 400 °C from PdA-PtO (a) and PdC-PtC (b).

**Table 3**

Effect of precursor and pretreatment on activity of catalysts in thiophene HDS.

Catalyst precursor	Pretreatment (gas/°C)	W (mg)	$x_{TH}$	$x_{THT}$	$x_{C4}$	$k_{TH}^a$ (mol <sub>TH</sub> /h.kg <sub>cat</sub> )
PdA-PtO	H300	9.1	0.90	0.09	0.81	34.0
	H400	8.5	0.86	0.11	0.75	29.1
	H550	9.0	0.84	0.11	0.73	28.1
	H600	9.1	0.82	0.11	0.71	24.6
	Ox400/H400	8.1	0.83	0.11	0.72	27.0
	He400/H400	7.5	0.84	0.11	0.73	32.7
	H300	9.2	0.80	0.19	0.61	21.8
PdA-PtC	H400	9.8	0.52	0.17	0.35	9.6
	He300/H300	9.5	0.77	0.23	0.54	18.6
PdC-PtC	H400	9.1	0.25	0.13	0.12	4.4
	Ox500/H400	9.8	0.87	0.14	0.73	26.0

<sup>a</sup> After 4 h on stream

**Table 4**

Effect of precursor and pretreatment on activity of catalysts in benzothiophene HDS. 330 °C, 1.6 MPa.

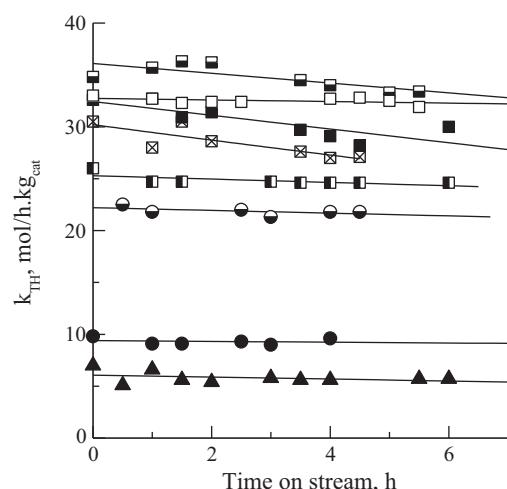
Catalyst precursor	Pretreatment (gas/°C)	W (mg)	$x_{BH}$	$x_{DHBT}$	$x_{EB}$	$k_{BT}$ (mol <sub>BT</sub> /h.kg <sub>cat</sub> )
PdA-PtO	H400	40	0.53	0.25	0.27	144
	H600	38	0.54	0.27	0.27	156
PdA-PtC	H300	40	0.57	0.33	0.24	161
	H400	40	0.35	0.17	0.18	82
PdC-PtC	H400	40	0.22	0.17	0.05	48
	Ox500/H400	40	0.65	0.31	0.34	205

the higher Pt fraction in this catalysts and also with the fact, that Pt showed a higher C–S bond hydrogenolysis activity than Pd [9]. The activity of all the catalysts was relatively stable during 4–6 h catalytic tests and only smaller deactivation was observed. The time dependences of  $k_{TH}$  are shown for some catalysts as examples in **Fig. 4**. Analogous data for BT reaction carried out with selected samples are given in **Table 4**. Also in this case, the transformation of BT was accompanied by the formation of an intermediate DHBT. Its amount was around 20–30% of the overall BT transformation and did not change significantly for different catalysts, similarly as in our preceding work [11].

### 3.2.1. Effect of precursor and pretreatment

**Table 3** shows that the activity of the catalysts in thiophene HDS is strongly influenced both by the precursor and by the way of pretreatment. The group of the catalysts prepared from PdA-PtO was by far more active, despite of the lowest metal loading. The pretreatment of PdA-PtO in air or helium at 400 °C prior to their reduction led to only small activity changes around 10%, compared to the direct reduction. On the other hand, the change of the reduction temperature had the greater effect. Its increase from 300 to 600 °C led to a progressive decrease of the activity by 30%. The maximum activity of PdA-PtO was thus achieved by the direct reduction at the lowest temperature of 300 °C. The same trends were observed with the PdA-PtC precursor. The sample directly

reduced at 300 °C was twice as active as that reduced at 400 °C, while pretreatment in helium led again to the activity similar to that for the reduced catalyst. The greatest activity change caused by pretreatment was observed with the PdC-PtC precursor.



**Fig. 4.** Rate constant of thiophene transformation ( $k_{TH}$ ) as a function of time on stream. Symbols same as in **Fig. 2**.

The catalyst prepared by calcination in air at 500 °C prior to its reduction gave five times more active sample than that directly reduced. The reason is undoubtedly prevention of an extensive sintering of the metallic phase during reduction, as confirmed by hydrogen sorption and EPMA analysis. Pre-oxidation of PdC-PtC suppressed such sintering and led to the highly active catalyst.

### 3.2.2. Sulfur tolerance of Pd-Pt/MSA catalysts

In order to obtain information about the state of the active phase during HDS, the Pd-Pt catalyst prepared from PdA-PtO and reduced at 400 °C was examined after TH reaction by ICP analysis and hydrogen sorption. For this purpose, HDS was carried out for 5 h at total TH conversion, which gave 240 ppm H<sub>2</sub>S in the reaction mixture. Then the catalyst was purged in hydrogen at 280 °C/1 h and atmospheric pressure in order to remove elemental sulfur. Treatment at this temperature should keep the state of the catalyst as close as possible to the reaction conditions. The ICP analysis showed that so treated catalyst contained 0.13 wt.% S. The dispersion of the sample was H/(Pd + Pt) = 0.12 (Table 2), which gave the sulfur coverage  $\Theta_S = (0.68 - 0.12)/0.68 = 0.82$ . This means that almost one fifth of the metal surface remained free, being close to the values evaluated by CO sorption for sulfided Pd-Pt/silica-alumina and Pd-Pt/USY zeolite catalysts [4]. In order to further find the effect of purging temperature on the sulfur coverage, a new 6 h run at total TH conversion was performed with the fresh PdA-PtO catalyst followed by purging in hydrogen at 400 °C/1 h. In this case, the catalyst showed much higher recovered metal fraction of 0.46, which corresponds to sulfur coverage  $\Theta_S = 0.32$ . The second purging of this catalyst by hydrogen at 400 °C/1 h led to an almost original dispersion value of 0.64, which corresponds to  $\Theta_S = 0.06$ . Such low values of sulfur coverage clearly show that most of the sulfur on Pd-Pt/MSA is deposited not strongly enough to be held irreversibly. This is an interesting quantitative result concerning Pd-Pt/MSA catalyst. Quite recently, Yu with coworkers [6] proposed that sulfur tolerance of Pd-Pt catalysts should increase at higher reaction temperatures. One of the reasons is an easier removal of sulfur deposited on the metallic phase by hydrogen reduction. The experiments performed now in the present work on a similar kind of Pd-Pt/silica-alumina catalyst nicely confirm such hypothesis.

There are numerous factors affecting the sulfur tolerance of bimetallic Pd-Pt catalysts, such as metal dispersion, alloying and interaction with the support, which all depend on preparation conditions [1 and 4 with References therein, 6]. High sulfur tolerance of the bimetallic catalysts is usually explained by high electron deficiency of noble metals after deposition on an acidic support or by their alloying. In the case of monometallic Pt catalysts their tolerance was found to correlate with the electronegativity of silica-alumina support being maximal at the alumina content 5–10% [35]. The exact reason of the high sulfur tolerance of our Pd-Pt/MSA catalysts is not at present known. We speculate that the overwhelming role is played by an optimal 9% alumina content, almost total absence of sodium (0.01 wt.% Na) after the acid leaching resulting in the strong Brønsted acidity, while the less important is probably metal alloying, at least in the case of PdA-PtO precursor. It can be summarized that around 20% of the accessible metal fraction remained free during tests with TH, which is most likely the reason for the relatively high and stable HDS activity documented in Fig. 4.

### 3.2.3. Metal dispersion, activity and hydrogen content in Pd-Pt catalysts

A well dispersed active phase is generally necessary to ensure the high activity of supported catalysts. This rule is well documented by the catalysts prepared from PdC-PtC by pre-oxidation in air at 500 °C prior to reduction. The oxidation leads to the reaction of chloride precursors with MSA surface forming anchored and dispersed oxide species, which keep their dispersion more or less also

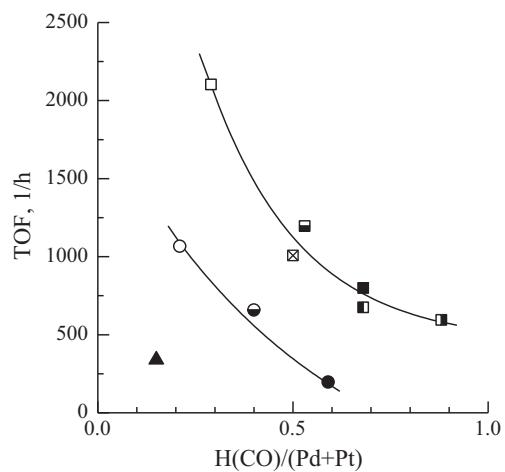


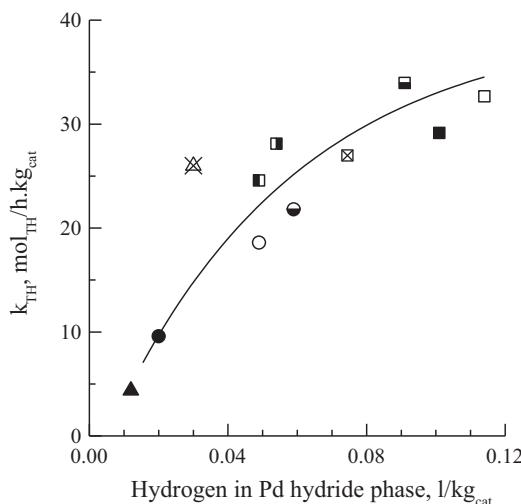
Fig. 5. Effect of overall metal dispersion on TOF values in thiophene HDS. Symbols same as in Fig. 2

after reduction. However, the pre-oxidation was not necessary for the catalysts prepared from the precursors containing Pd acetate. In those cases, good dispersions or activities in TH reaction were achieved by direct reduction as well as by treatment in helium. As already shown, the dispersion of the catalyst series prepared by the reduction of PdA-PtO shows a maximum after reduction at 550 °C (Table 2), while thiophene HDS activity continuously diminished with increasing reduction temperature (Table 3). This indicates the absence of any straightforward relation between the dispersion of the active metal phase and catalyst activity.

In attempt to get a deeper insight in this problem, the specific rate constants  $k_{TH}$ , expressed per mol of deposited metals were plotted against the  $H(CO)/(Pd+Pt)$  ratios. However, these values suffered from larger fluctuations (not shown). Thus, in the next, the TOF values considering only accessible metal atoms, were correlated with the  $H(CO)/(Pd+Pt)$  ratios in Fig. 5. In this case, fairly convincing dependences were obtained for both catalyst series prepared from PdA-PtO and PdA-PtC. These data are interesting from the two aspects. First, they allow compare the efficiency of the catalytic sites originating from different precursors at the same overall metal dispersion. From this point of view, the most active sites in TH reaction are created from PdA-PtO precursor, followed by PdA-PtC and PdC-PtC. It is also of interest that the most active sites are formed on the catalysts pretreated in helium. Secondly, the better dispersed is the metal phase, the lower the TOF values are. This fact seems to contradict to the result obtained with the PdC-PtC precursor, but can be rationalized taking into account the ability of Pd particles to absorb hydrogen.

Formal similarity of the dependences is apparent from comparison of Fig. 2 and Fig. 5 and suggests that there exists some relation between hydrogen content held by PdH<sub>x</sub> phase and thiophene HDS activity. Fig. 6 shows the relation between  $k_{TH}$  and the amounts of hydrogen absorbed in the catalysts. The existence of such a relation confirms clearly the positive role of hydrogen absorbed in PdH<sub>x</sub> during TH reaction over Pd-Pt/MSA catalysts. It can be proposed that this phase obviously partly serves as a storage medium controlling the delivery of some fraction of the activated hydrogen in HDS reaction. In this case, it plays a role similar to that proposed for hydrogenation of alkynes and alkenes over Pd metal [12,14,16] or Pd/Al<sub>2</sub>O<sub>3</sub> catalyst, observed earlier by other workers [13].

As already discussed in Section 3.1, the catalysts prepared from PdC-PtC and PdA-PtC contained chlorine and also showed lower TOF than PdA-PtO samples, which could suggest its possible inhibiting effect. It is known that chlorine diminished the activity of catalysts in various reactions such as oxidation, water gas shift

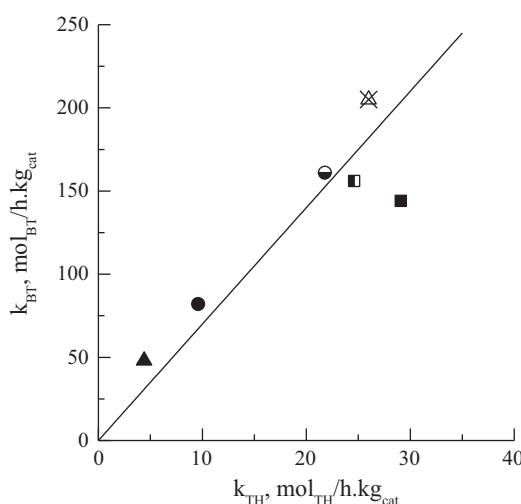


**Fig. 6.** Correlation of  $k_{TH}$  on the amount of hydrogen absorbed in  $PdH_x$  phase of Pd-Pt/MSA catalysts. PdC-PtC; Ox 500/H400 (×). Other symbols same as in Fig. 2.

or HYD. On the other hand, positive effect of residual chlorine was observed in HDS of 4,6-dimethylbenzothiophene and HYD of tetraline over Pd-Pt/USY zeolite catalyst prepared from Pd and Pt tetraamine chlorides and explained by higher sulfur tolerance of this catalyst as compared to catalyst prepared from Pd and Pt tetraamine acetates [4]. In the present work, the question of a possible effect of chlorine on activity still remains open. Such problem needs a further study with quantitative characterization of its amount and forms in the catalysts.

### 3.2.4. Comparison of activities in reactions of thiophene and benzothiophene

Distinct positive effects of the pretreatment of the precursor observed in TH reaction were also verified in the reaction of heavier BT molecule. The most important were the effects of the lower reduction temperature of 300 °C and the pre-oxidation of PdC-PtC precursor. Fig. 7 shows the relation between the rate constants  $k_{TH}$  and  $k_{BT}$  for some selected catalysts. A straight line fitting the majority of experimental points confirms that the effects observed in TH reaction also hold for transformation of BT. Lowering of the reduction temperature of PdA-PtC by 100 °C gave in both reactions approximately twofold activity. Similarly, the pre-oxidation of



**Fig. 7.** Relation between the rate constants for overall transformation of BT and TH. Symbols same as in Fig. 2 and 6.

PdC-PtC even led to the greater activity improvement, giving the most active catalyst in BT reaction.

## 4. Conclusions

The catalyst precursor and its pretreatment significantly affected the properties of the reduced Pd-Pt/MSA catalysts in HDS of thiophene and benzothiophene. The most active catalysts were prepared from Pd acetate and  $Pt(NH_3)_4(OH)_2$ . Their activities were only slightly influenced by the way of pretreatment. The less active catalysts were prepared when  $PdCl_2$  and  $H_2PtCl_6$  were used as the precursors. However, their activity was more sensitive to pretreatment. This is probably due to weaker interactions of  $PdCl_2$  and  $H_2PtCl_6$  with highly siliceous MSA surface, allowing their partial segregation and metal sintering during their reduction in hydrogen atmosphere. On the other hand, an optimum composition and strong acidity of the support most likely led to high sulfur tolerance of Pd-Pt/MSA catalysts; around 20% of the active phase remained free as metals after HDS reaction. Moreover, the sulfur-metal bond was not strong enough to keep sulfur irreversibly. This allowed the removal of great part of deposited sulfur by hydrogen at 400 °C and substantial recovery of the metal surface.

The bimetallic Pd-Pt/MSA catalysts absorbed hydrogen in the form of  $\beta$ -Pd hydride ( $PdH_x$ ). Its amount strongly depended on the catalyst precursor, its pretreatment and overall metal dispersion. A relation between amount of this hydrogen and thiophene transformation activity of the catalysts was obtained. It was proposed that the interaction of Pt and Pd led to the accumulation of the activated hydrogen in the  $PdH_x$  phase, which most likely served as a storage medium delivering some part of hydrogen in the reaction. This subsurface hydrogen, in addition to a common surface hydrogen activation, obviously contributed to the higher overall thiophene transformation over some Pd-Pt/MSA catalysts. This mechanism was mostly effective on the catalysts prepared from the chlorine free Pd acetate and  $Pt(NH_3)_4(OH)_2$ .

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